Appendix 2

"Free Volume Variation with Molecular Weight of Polymers" J. J . Singh, Abe Eftekhari, Jeffrey A Hinkley, Terry L. St. Clair, and Brian J. Jenson, NASA Tech. Memo. 4326 (Feb (1992).

NASA Technical Memorandum 4326

Free Volume Variation With Molecular Weight of Polymers

Jag J. Singh
Langley Research Center
Hampton, Virginia

Abe Eftekhari
Hampton University
Hampton, Virginia

Jeffrey A. Hinkley, Terry L. St. Clair,
and Brian J. Jensen
Langley Research Center
Hampton, Virginia

Abstract

Free volume measurements have been made in several molecular weight fractions of two different geometries of poly(arylene ether ketone)s. Free volumes were measured using positron lifetime spectroscopy. It has been observed that the free volume cell size V_f varies with the molecular weight M of the test samples according to an equation of the form $V_f = AM^B$, where A and B are constants. The molecular weights computed from the free volume cell sizes are in good agreement with the values measured by gel permeation chromatography.

Introduction

All polymers generally have regions of low atomic density (free volume cells) resulting from geometrical mismatch among neighboring molecular chains/segments. The sizes and concentrations of these free volume cells depend on the polymer molecular architecture and affect many physical properties of high polymers. For example, we have recently shown (ref. 1) that both the solubility coefficient as well as the diffusion coefficient for gaseous molecules are modified by the presence of free volume cells in the test polymers. As a result, the presence of free volume cells in the test polymers enhances the permeation of gases through them. Similarly, the free volume cells in polymeric materials affect their other thermodynamic properties. The free volume cell sizes change markedly at the phase transition temperatures of the test polymers. Thus, the large differences in thermal expansion coefficients observed above and below the glass transition temperatures arise from the large free volume expansion at the glass transition temperatures. The rapid decrease of free volume cell size with increase in pressure above the glass transition temperature also accounts for the observed trends in the compressibility of polymeric materials as a function of temperature. It is also noted that positron lifetime spectroscopy separates free volume compressibility from the compressibility of the excluded volume of the test polymers. Many conventional techniques can yield (ref. 2) only a total compressibility that includes both effects.

It thus appears that the free volume plays an important role in determining physical properties of the polymeric materials. In the case of linear polymers, a relationship between the free volume cell size and the molecular weight of the polymer can be developed. Let the molecular weight of the polymer be M. Then n moles of the polymer shall weigh $nM = M_1$ and

$$M_1 = \rho V \qquad (1)$$

where ρ is the density of the polymer and V is the volume occupied by the polymer when it has zero free volume.

If the polymer has a free volume ΔV then the total volume occupied by the polymer is $V + \Delta V$. Then we have

$$M_1' = \rho V + \rho'(\Delta V) \qquad (2)$$

where ρ' is the density of the medium occupying ΔV. Equation (2) can be rearranged as follows:

$$M_1' = \rho V \left(1 + \frac{\rho'}{\rho}\frac{\Delta V}{V}\right)$$
$$= \rho V \left(1 + \alpha\frac{\Delta V}{V}\right) \qquad (3)$$

where $\alpha = \rho'/\rho$ = Constant for a polymer system. Rewriting equation (3), we have

$$M_1 + \Delta M_1 = M_1\left(1 + \alpha\frac{\Delta V}{V}\right)$$
$$\frac{\Delta M_1}{M_1} = \alpha\frac{\Delta V}{V}$$
$$\frac{\Delta M}{M} = \alpha\frac{\Delta V}{V} \qquad (4)$$
$$\frac{\Delta M}{M} = \alpha f \qquad (5)$$

where f = Free volume fraction = CI_3V_f, C is the polymer structural constant, I_3 is the intensity of the third (longest) positron lifetime component, and V_f is the free volume cell size. Thus, equation (5) becomes

$$\frac{\Delta M}{M} = (\alpha C)I_3V_f$$
$$= (\beta I_3)V_f \qquad (6)$$

where $\beta = \alpha C$. Since I_3 and V_f are independent variables, equation (6) can be written as follows:

$$\psi_1(M) = D\psi_2(V_f) \qquad (7)$$

where $D = \beta I_3$ is a constant related to electron density/momentum distribution and the architecture of the test polymer. It thus appears that the free volume cell size V_f is a function of M. The relationship between V_f and M can be expressed as follows:[1]

$$V_f = AM^B \qquad (8)$$

---

[1] Preliminary results based on this formalism have been reported previously. (See ref. 3.)

where A and B are constants for the test polymer and are expected to be independent of its degree of polymerization. However, they depend on the temperature and pressure of the sample environment.

Equation (8) is quite similar in form to the Mark-Houwink equation relating the intrinsic viscosity $[\eta]$ and the molecular weight M of the polymer in solution (ref. 4). It can be extended to cross-linked polymers if M represents the weight of the polymer sample between two adjacent cross links. The purpose of this study is to make a systematic investigation of V_f versus M in selected linear polymers. Poly(arylene ether ketone)s (PAEK) of variable molecular weights were selected as the test polymers. The free volume V_f values were measured using positron lifetime spectroscopy (PLS). All measurements were made at room temperature and atmospheric pressure.

Experimental Procedure

Sample Preparation

The structures of poly(arylene ether ketone)s chosen for study are shown in figure 1. It was anticipated that the different geometries of the two repeat units might lead to different packing behaviors and hence different free volumes. Details of their syntheses and fractionation have been reported earlier (ref. 5). Several molecular weight fractions were studied in an effort to discern possible effects of chain ends. Molecular weights of the various fractions differed by over a factor of 4, although, as nearly as could be determined, the specific volumes of both polymers were practically independent of molecular weights in this range (table I).
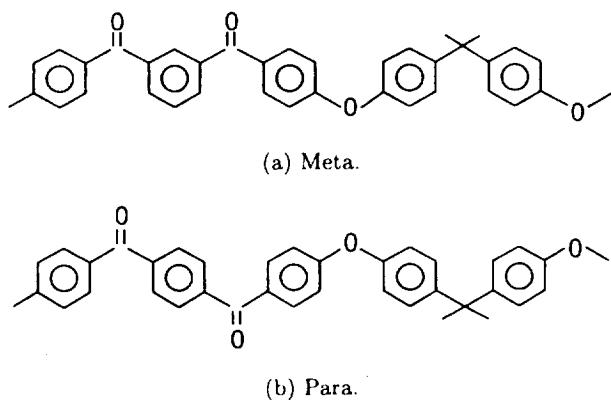

(a) Meta.

(b) Para.

Figure 1. Structure of meta- and para-poly(arylene ether ketone)s.

Thin (30 μm) films for the positron lifetime studies were prepared by casting them on glass plates

from m-cresol solution. These films were air dried for 2 days in a low-humidity enclosure, then gradually heated in an air-circulating oven to 250°C, which is well above the polymer glass transition temperature T_g. Finally, they were cooled rapidly to room temperature by removing the plates from the oven and placing them on a cool surface. Wide angle X-ray scattering showed the films to be free of detectable crystallinity.

Positron Lifetime Measurements

Positron lifetime measurements were made using a standard fast-fast coincidence timing technique. The coincidence system time resolution was of the order of 225 psec. All measurements were made at room temperature and atmospheric pressure. Typical spectrum accumulation time was $\approx$6 hr with a 50 μc Na^{22} positron source. This accumulation time provided excellent counting statistics—namely 10^6 counts in the peak channel. Figure 2 shows a typical lifetime spectrum in para-PAEK films. Figure 3 shows a typical spectrum in meta-PAEK films. Lifetime spectra were analyzed using PAPLS (ref. 6) and POSITRONFIT EXTENDED (ref. 7) computer programs. In all cases, three-component analyses gave the best fits to the experimental spectra.

Experimental Results

Results in PAEK Films

The positron lifetime results in para-PAEK films are summarized in table II; τ_1, I_1 and τ_2, I_2 refer to the lifetime and intensity of the first and second components, respectively. The longest component lifetime (τ_3) results from orthopositronium annihilation. The lifetime (τ_3) and its intensity (I_3) are related to the free volume cell size V_f as follows (ref. 8):

$$\frac{1}{2\tau_3} = \left(1 - \frac{R}{R_o} + \frac{1}{2\pi}\sin\frac{2\pi R}{R_o}\right) \qquad (9)$$

where

τ_3 longest component lifetime, nsec

R free volume cell radius, nm

R_o $= (R + \Delta R)$, nm

(The best fitted value of ΔR for all known data has been reported to be 0.1659 nm. See ref. 8.)

The free cell volume V_f is given by $\frac{4}{3}\pi R^3$. The V_f values for various para-PAEK samples are summarized in table III. The positron lifetime results in meta-PAEK films are summarized in table IV. The corresponding V_f values are summarized in table V.
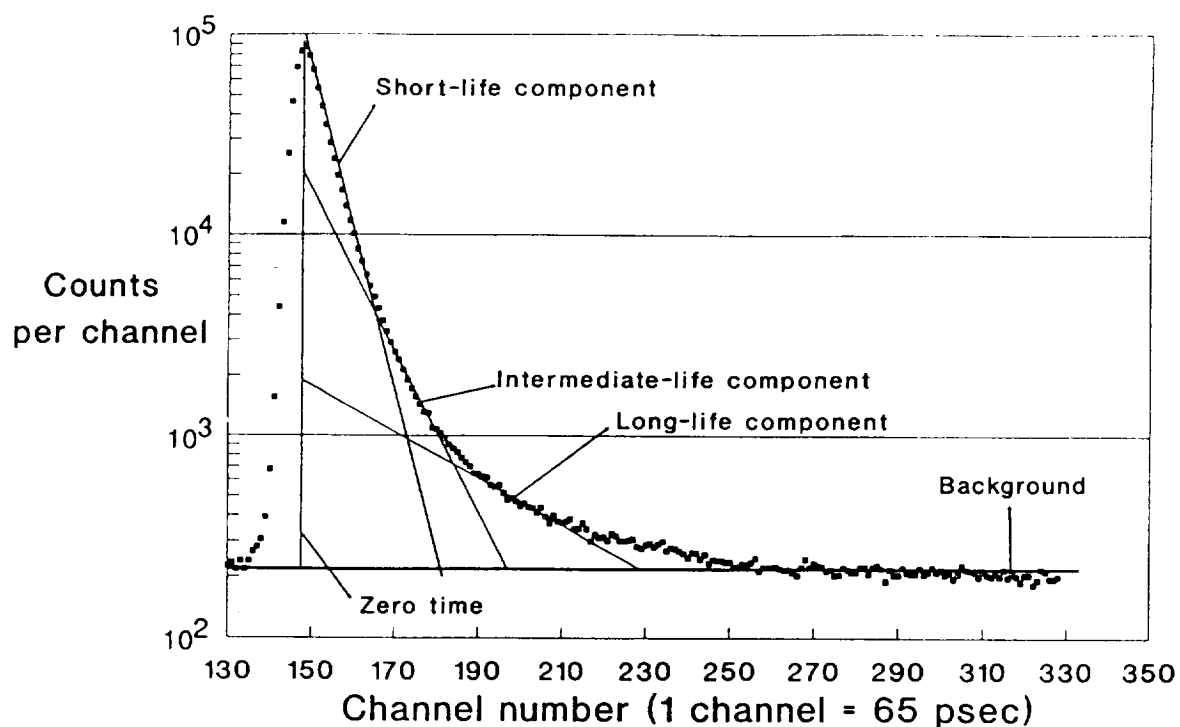
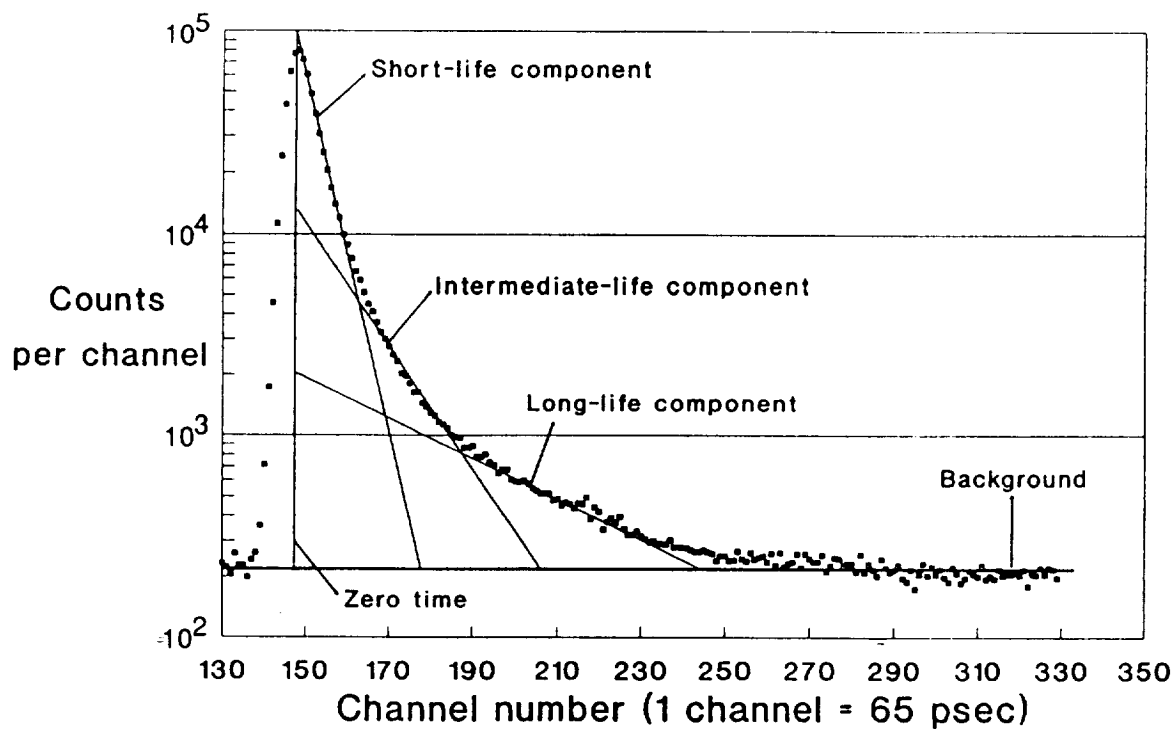Figure 2. Typical lifetime spectrum in para-PAEK films.

Figure 3. Typical lifetime spectrum in meta-PAEK films.

In addition to the values of V_f, measured values of saturation moisture content v/o in the test films have also been included in tables III and V.

The free volume fraction f in the test films can be calculated as follows:

$$f = CI_3V_{f3} \qquad (10)$$

where V_{f3} is the free volume cell size associated with the third lifetime component.

If one assumes that water enters the test films physically, the values of C can be easily calculated by equating f with the corresponding saturation moisture content v/o. This, however, may not always be the case. In some cases, the presence of hydrophobic atoms in the polymer chains may inhibit water entry in the free volume cells, as reported by Singh et al. in a recent study of contact lens polymers (ref. 1). In others, water may enter the polymer system chemically as well as physically, thus making the saturation moisture content v/o exceed the free volume fraction (ref. 9). A small concentration of microdefects above the size of the PLS limit ($R \geq 5$ Å) can also cause v/o to exceed f. Nevertheless, v/o should often provide a good first-order approximation for f.

Calculation of the Molecular Weights

In order to obtain the values of A and B in equation (8), experimental values of the molecular weights (M_n) of the test films were determined using the gel permeation chromatography/low angle laser light scattering (GPC/LALLS) technique (ref. 5). There were five para-PAEK samples and three meta-PAEK samples of different molecular weights. We used experimental molecular weights of three para-PAEK samples to determine the constants A and B by least-squares method. These constants were then used to predict the molecular weights of the remaining two samples. Similarly, two experimental molecular weights of the meta-PAEK samples were used to determine the structural constant A. The constant B is expected to remain unchanged.[2] The meta A and B combination of constants was then used to predict the molecular weight of the third meta sample. Comparisons between the experimental and calculated M_n values for the two systems are summarized in tables III and V, respectively. It is apparent that the agreement is quite good for both polymer systems. This indicates that equation (8) represents

the correct form of relationship between V_f and M. The results are illustrated in figure 4.

Equation (8) should be applicable for the entire range of orthopositronium lifetimes observed in linear polymers—namely, 0.7–3.5 nsec. These lifetimes correspond to molecular weights ranging from 4000 to 200 000 g/mole.

Discussion

From the data presented above, it appears that V_f values track the M_n values of the test polymers quite well. As expected, a unique set of A and B values predict the test polymer M_n values as long as their molecular structure remains unchanged. A change in structure as we go from para-PAEK to meta-PAEK necessitates a different set of constants. A notable feature is the fact that V_f values are much larger in the meta geometry than the para geometry. However, this is consistent with the different packing behavior of the two geometries.

It has been reported (ref. 10) that as the molecular weights of most linear polymers decrease, their free volumes increase. The free volume fraction is given by CI_3V_f, as indicated in equation (10). It would thus appear that I_3V_f would decrease with increasing molecular weight of the test samples. This, however, is not the case in the samples investigated. Similarly, the trend in the change in the specific volume ($1/\rho$) with the molecular weight is also contrary to the reported behavior (ref. 10). Thus, both the I_3V_f and $1/\rho$ values exhibit trends with increasing molecular weights that are contrary to the reported behavior in most linear polymers. The glass transition temperatures T_g, on the other hand, increase with increasing molecular weights in agreement with the reported trends (ref. 10). These results are quite intriguing, though not inconsistent with the morphologies of the test polymers.

A further corroboration of the validity of the Free Volume Model was obtained by comparing the Mark-Houwink (M-H) (ref. 3) and Free Volume Model constants. The results are summarized in table VI. Clearly, the M-H and Free Volume Model exponential constants exhibit similar behavior when the repeat unit geometries change.

Concluding Remarks

It has been demonstrated that positron lifetime spectroscopy (PLS) may provide a reasonably accurate technique for measuring molecular weights of polymeric materials. However, the number of test samples in the present study was rather limited. The proposed model will have to be tested on a larger

---

[2] By considering all five para-PAEK and all three meta-PAEK samples, it has been determined that the constant B is the same for all PAEK samples, as expected from the theoretical arguments presented earlier.
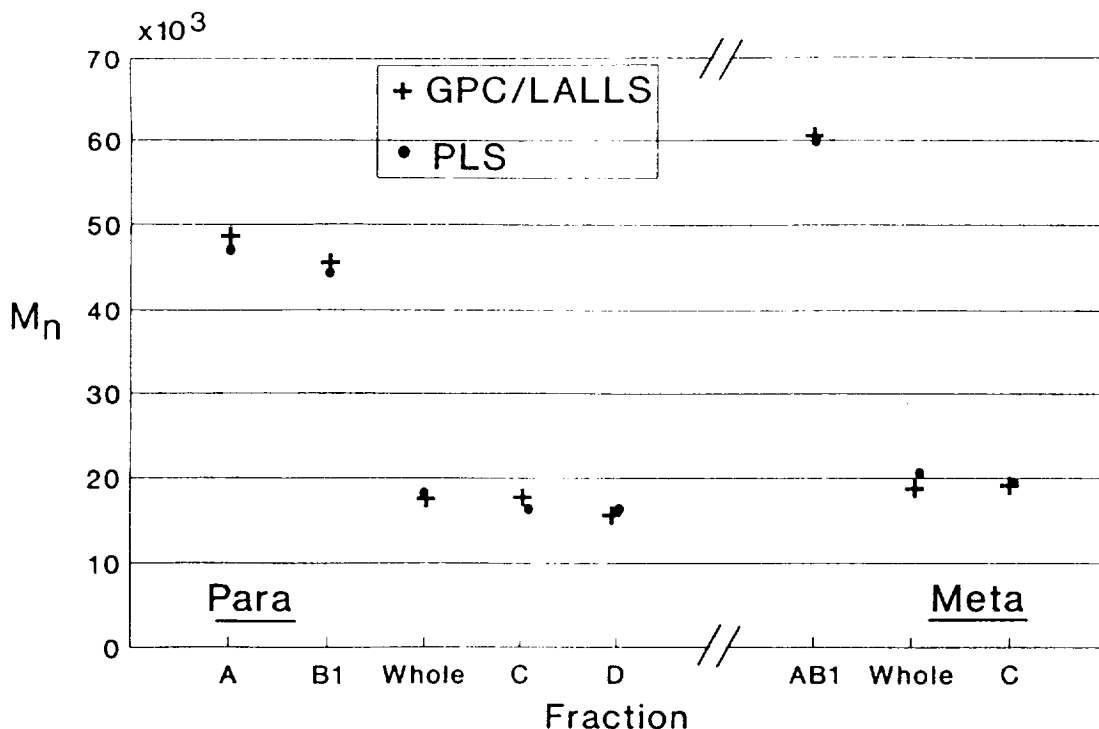
Figure 4. Comparison between molecular weights determined by GPC/LALLS and PLS methods.

number of a variety of samples before it becomes accepted. The proposed technique relates the free volume cell size V_f with the sample molecular weight M in a manner remarkably similar to that obtained by Mark-Houwink (M-H) relating the inherent viscosity $[\eta]$ and the molecular weight of the polymer solution. However, the M-H procedure requires the sample to be in liquid form. The PLS technique has been verified for two geometries of the poly(arylene ether ketone)s, where it not only predicts, with reasonable accuracy, the higher V_f values (i.e., looser packing) for the meta geometry, but also verifies anticipated structural change.

NASA Langley Research Center
Hampton, VA 23665-5225
December 20, 1991

References

1. Singh, Jag J.; Eftekhari, Abe; Upchurch, Billy T.; and Burns, Karen S.: Free Volume in Contact Lens Polymers. *Third International Workshop on Positron and Positronium Chemistry*, Y. C. Jean, ed., World Scientific Publ. Co., Inc., 1990, pp. 54–61.

2. Jean, Y. C.: Free-Volume Hole Properties of Polymers Probed by Positron Annihilation Spectroscopy. *Third International Workshop on Positron and Positronium Chemistry*, Y. C. Jean, ed., World Scientific Publ. Co., Inc., 1990, pp. 1–29.

3. Singh, Jag J.; Eftekhari, Abe; and St. Clair, Terry L.: *A Study of Physical Properties of ODPA-p-PDA Polyimide Films*. NASA TM-102625, 1990.

4. Seymour, Raymond B.; and Carraher, Charles E., Jr.: *Structure-Property Relationships in Polymers*. Plenum Press, c.1984.

5. Hinkley, J. A.; Crook, R. A.; and Davis, J. R. J.: Chain Dimensions and Rheology of Poly(arylene ethers). *High Perform. Polymers*, vol. 1, no. 1, 1989. pp. 61–71.

6. Singh, Jag J.; Mall, Gerald H.; and Sprinkle, Danny R.: *Analysis of Positron Lifetime Spectra in Polymers*. NASA TP-2853, 1988.

7. Kirkegaard, P.: Positronfit Extended: A New Version of a Program for Analysing Positron Lifetime Spectra. *Comput. Phys. Commun.*, vol. 7, no. 7, July 1974, pp. 401–409.

8. Nakanishi, H.; Wang, S. J.; and Jean, Y. C.: Microscopic Surface Tension Studied by Positron Annihilation. *International Symposium on Positron Annihilation Studies of Fluids*, Suresh C. Sharma, ed., World Scientific Publ. Co., Inc., 1988, pp. 292–298.

9. Singh, Jag J.; St. Clair, Terry L.; Holt, William H.; and Mock, Willis, Jr.: Moisture Dependence of Positron Annihilation Spectra in Nylon-6. *Nucl. Instrum. & Methods Phys. Res.*, vol. 221, no. 2, Apr. 1, 1984, pp. 427–432.

10. Liu, Xijun; Chen, Donglin; He, Zhiduan; Zhang, Hao; and Hu, Huizhen: Molecular Weight Dependence of Glass Transition of Cyclic Polystyrene. *Polymer Commun.*, vol. 32, no. 4, 1991, pp. 123–125.

Table I. Characteristics of Polymer Fractions (ref. 5)

Sample	$^*M_n$	$^\dagger M_n$	M_w	ρ, g/cm^3	η_{inh}, dl/g	T_g, °C
Para						
Whole polymer		19.0×10^3	26.0×10^3	1.2058	0.50	
Fraction A	29.6×10^3	47.0	51.0	1.2060	.78	165
Fraction B1	28.4	44.5	45.9	1.2041	.70	163
Fraction C	15.4	17.6	18.3	1.2052	.37	159
Fraction D	17.8	16.3	16.9	1.2061	.38	160
Meta						
Whole polymer		20.8×10^3	26.6×10^3	1.2072	0.39	148
Fraction AB1	47.3×10^3	60.8	66.0	1.2077	.65	153
Fraction C	20.3	19.8	21.0	1.2074	.35	148

*End group analysis.

†Gel permeation chromatography/low angle laser light scattering technique. These values have an error of ±10 percent.

Table II. Positron Lifetime Parameters in Para-Poly(Arylene Ether Ketone) Films

Geometry	τ_1, psec	I_1, %	τ_2, psec	I_2, %	τ_3, psec	I_3, %
Whole polymer	187 ± 12	37 ± 3	409 ± 16	59 ± 3	905 ± 60	4 ± 1
Fraction A	171 ± 09	44 ± 3	407 ± 16	53 ± 2	1069 ± 70	3 ± 1
Fraction B1	139 ± 16	35 ± 4	371 ± 24	60 ± 2	1037 ± 70	6 ± 1
Fraction C	196 ± 08	41 ± 2	416 ± 20	56 ± 3	869 ± 75	3 ± 1
Fraction D	165 ± 17	33 ± 5	390 ± 24	63 ± 3	850 ± 65	4 ± 1

Table III. Summary of V_f Values in Para-Poly(Arylene Ether Ketone) Films

Sample	$^*M_n$	V_f, Å^3	$^{**}M_n$
†Whole polymer	19.0×10^3	13.7 ± 0.6	$(21.3 \pm 1.5) \times 10^3$
†Fraction A	47.0	23.2 ± 0.7	51.3 ± 2.4
‡Fraction B1	44.5	21.3 ± 0.6	43.2 ± 1.9
‡Fraction C	17.6	12.1 ± 0.8	17.5 ± 1.9
†Fraction D	16.3	11.2 ± 0.9	15.5 ± 2.0

$^*M_n$ values were determined by gel permeation chromatography/low angle laser light scattering technique. All values have an error of ±10 percent.

$^{**}M_n$ values are calculated by using the equation $V_f = AM_n^B$, where $A = 2.70 \times 10^{-2}$ and $B = 0.625$.

†These three samples were used to calculate the constants A and B.

‡The molecular weights of these samples were calculated using the values of A and B computed above.

Table IV. Positron Lifetime Parameters in Meta-Poly(Arylene Ether Ketone) Films

Geometry	τ_1, psec	I_1, %	τ_2, psec	I_2, %	τ_3, psec	I_3, %
Whole polymer	183 ± 4	51 ± 2	442 ± 8	43 ± 1	1698 ± 40	6 ± 1
Fraction AB1	211 ± 3	59 ± 1	516 ± 23	36 ± 1	2273 ± 77	5 ± 1
Fraction C	181 ± 7	46 ± 3	433 ± 12	47 ± 2	1651 ± 52	7 ± 1

Table V. Summary of V_f Values in Meta-Poly(Arylene Ether Ketone) Films

Sample	*M_n	V_f, Å^3	**M_n
‡Whole polymer	20.8×10^3	70.8 ± 0.4	$(22.8 \pm 0.2) \times 10^3$
†Fraction AB1	60.8	130.2 ± 0.4	60.3 ± 0.3
†Fraction C	19.8	66.2 ± 0.6	20.4 ± 0.3

*M_n values were determined by gel permeation chromatography/low angle laser light scattering technique. All values have an error of ±10 percent.

**M_n values are calculated by using the equation $V_f = AM_n^B$, where $A = 1.340 \times 10^{-1}$ and $B = 0.625$.

†These two samples were used to calculate the constant A.

‡The molecular weight of this sample was calculated using the value of A computed above.

Table VI. Summary of Mark-Houwink and Free-Volume Equation Constants

$$\begin{bmatrix} \text{Mark-Houwink Equation:} & [\eta] = KM^a \\ \text{Free Volume Model:} & V_f = AM^B \end{bmatrix}$$

Sample	Mark-Houwink equation		Free-volume model	
	K	a	A	B
Para-PAEK	1.20×10^{-3}	0.60	2.70×10^{-2}	0.625
Meta-PAEK	9.00×10^{-4}	0.60	1.34×10^{-1}	0.625